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THERMOLYSIS OF FIBREGLASS POLYESTER COMPOSITE AND REUTILISATION OF THE GLASS FIBRE RESIDUE TO OBTAIN A GLASS-CERAMIC MATERIAL

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ABSTRACT

This study reports the feasibility of reusing glass fibre waste resulting from the thermolysis of polyester fibreglass (PFG) to produce a glass-ceramic material. PFG was treated at 550ºC for 3 h in a 9.6 dm^3 thermolytic reactor. This process yielded a solid residue (≈68 wt.%), an oil (≈24 wt.%) and a gas (≈8 wt.%). The oil was mainly composed of aromatic (≈84%) and oxygenated compounds (≈16%) and had a fairly high gross calorific value (≈34 MJ kg^{-1}). The major PFG degradation products were styrene, toluene, ethylbenzene, α-methyl styrene, 3-butynyl benzene, benzoic acid and 1,2-benzenedicarboxylic acid anhydride. The gas contained basically CO_2 and CO; the hydrocarbon content was below 10 vol%. The higher gross calorific value of the gas was low (26 MJ Nm^{-3}). The solid residue (97 wt% fibreglass, 3 wt% char) was converted into a glass-ceramic material. For this, a mixture consisting of 95 wt% of this solid residue and 5% Na_2O was melted at 1450ºC to obtain a glass frit. A powder glass sample (<63 μm) was then sintered and crystallized at 1013ºC, leading to the formation of a glass-ceramic material composed of wollastonite and plagioclase s.s. with possible building applications.

Keywords: Thermolysis; Polyester fibreglass; Glass fibre; Vitrification; Glass-ceramic material

1. Introduction

Fibreglass is the most commonly used reinforcement in the manufacture of composite materials with polymeric matrices. The matrix of fibreglass is composed of organic, thermostable polyester, vinylester, phenolic and epoxy resins. Polyester resins, which are essentially bisphenolic and ortho- or isophtalic, make up some 75% of this matrix.

Fibreglass reinforced plastics (FGRP) have important applications in the fields of automobile manufacturing, aeronautical industry, and in civil, mechanical and biomechanical engineering. Their properties compare favourably with those of other materials and they are sometimes used on an exclusive basis. In 2010, the total production of FGRP materials in Europe reached 1015 Mt [1].

Recycling composites is difficult since they typically contain two or more components (filler, fibre, resin, etc.). Recycling thermoset composites is a particular challenge since, once the thermoset matrix molecules are cross-linked, the resulting material can no longer be remelted or remoulded [2]. Further, the most common thermosetting resins, such as polyester and epoxy resin, cannot be depolymerised to their original constituents [3]. Thermoset composites therefore commonly end up in landfills, and since the components are non-biodegradable, the economic costs of such disposal can be very high.

A number of technologies have been proposed for recycling thermoset composites. Basically, these can be classified into three categories:

a) Mechanical comminution-based processes to obtain a specific grain size that renders the material useful as a reinforcement in new formulations [4-6].
b) Thermal processing such as:
   (i) Combustion and the use of the heat generated [7-8]. The combustion of fibreglass composite waste in a cement kiln is one option. The thermosetting resin acts as fuel within the kiln, while the glass reinforcement and mineral fillers are incorporated into the cement as valid raw materials [9-10].
   (ii) Pyrolysis i.e., the chemical decomposition of the organic matter by heating at moderate temperature in the absence of oxygen. Such processes produce a fuel gas which can be used for heating the pyrolysis chamber itself. It also generates certain liquid oil products and a solid residue comprised of inorganic fibres, filler and char [11-14]. Thermolysis, a

type of pyrolysis involving the thermal decomposition of organic materials at moderate temperatures in a 3-7% oxygen atmosphere (insufficient to allow combustion), has been successfully used to recycle scrap tyres [15].

(iii) Fluidised bed thermal processes to recover the carbon fibre reinforcement from composites [16-19].

c) Composite depolymerisation based on chemical processes such as hydrolysis, glycolysis and solvolysis to recover organic materials [20-22].

Unfortunately, the glass fibres obtained as a solid residue in pyrolysis suffer the degradation of their physical properties, limiting their reuse. Pickering [3] and Pickering et al. [17] reported a 50% reduction in the compressive strength of the fibres derived from pyrolytic processing of a sheet moulding compound (SMC) involving a fluidised bed. Nonetheless, the residual glass fibre was used in the manufacture of new composites (polyester dough moulding compound) with no important decline in the mechanical properties of the final product. Some 25% of the original glass fibre was recycled. Recently, Jie et al. [23] reported a 35% reduction in the tensile strength of glass fibres recovered from printed circuit boards (made of epoxy resins reinforced with fibreglass) via pyrolysis in a tubular reactor at 450ºC. Torres et al. [24], however, who used a solid residue (glass fibre and $CaCO_3$) obtained from the pyrolysis of an SMC material at 500 ºC as a replacement for original fibre and filler in the manufacture of a bulk moulding compound (BMC), found that the physical properties of the latter were not negatively affected by a residue inclusion rate of 6%. Nonetheless, none of these techniques achieves more than the partial recovery of glass fibre and packing.

The present work is the first to propose the reuse of glass fibre in the production of a glass-ceramic material. Glass-ceramics are polycrystalline materials of fine microstructure that are produced by the controlled crystallisation (devitrification) of a glass. The first glass-ceramics, developed in the 1950s, were produced via a conventional glass-making process, followed by crystallisation involving heating and later cooling (allowing nucleation and crystallisation respectively). In recent years, however, sintering has become a technologically viable route of glass-ceramic manufacture. Sintered glass-ceramics are usually made by milling a glass frit into particles of adequate size, heating to induce sintering, and then allowing crystallisation.

Glass-ceramics have found a wide variety of applications in different technological fields [25]. The most important glass-ceramic for building applications is Neoparies®. This wollastonite material is produced on a large scale for building interior and exterior walls. Large flat or curved sheets of this material can also be produced for facing buildings. The main properties of Neoparies® include great resistance to weathering, zero water absorption rate, hardness (which is greater than that of natural stone), light weight (30% lighter than natural stone building materials), and the ease with which curved panels can be made.

Cryston® is another wollastonite glass-ceramic that can be used as an architectural covering material. The chemical durability of Cryston® is very high, its chemical properties being nearly the same as those of float glass [25].

This paper proposes the valorisation of polyester fibreglass (PFG) waste via thermolysis and the subsequent use of the residual glass fibre as a precursor for the manufacture of a wollastonite-plagioclase glass-ceramic material for architectural applications.

2. Materials and Methods

2.1. Polyester fibreglass waste characterisation

The PFG waste (Polifibra S.A., Guadalajara, Spain) used in this work was exclusively composed of E-fiberglass (SiO_2: 54.3 wt%; Al_2O_3: 15.2 wt%; CaO: 17.2 wt%; MgO: 4.7 wt%; B_2O_3: 8.0 wt%) plus unsaturated polyester resin made from orthophtalic acid and styrene. The curing agent for the unsaturated polyester resin was a combination of methyl ethyl ketone peroxide (2 wt% of the resin) and cobalt octoate (0.2 wt% of the resin). Table 1 shows the composition (manufactured material) of PFG waste used in the experiments. The total amount of organic matter contained in such PFG waste, deduced from Table 1, is 35.5 wt%; this percentage should correspond to the amount of gases + liquids to be obtained in the thermolisis tests and consequently a solid residue, basically composed of fibre-glass, of 64.5 wt.% should be obtained. The PGF waste used in this work contained no filler.

The elemental composition of the PFG waste were determined using an automated LECO CHNS 923 analyser (Table 2). A GCV of 9.6 MJ kg^{-1} was estimated for the PFG waste, derived from the value of the pure resin (26.96 MJ kg^{-1}) [26].

Table 1 Composition of the PFG waste used in the present experiments (wt%).

Component	Ortho-phthalic polymer resin	Organic catalyst	Styrene monomer	Zn stearate lubricant	Fiber-glass
Proportion (wt.%)	32.8	0.3	1.2	1.2	64.5

Table 2 Elemental composition (wt%) and gross calorific value (MJ kg^{-1}) of the PFG waste and recycled glass fibre obtained by thermolysis.

	C (wt%)	H (wt%)	O[a] (wt%)	N (wt%)	GCV (MJ kg^{-1})
PGF waste	22.9	1.5	10.6	0	9.6[b]
Glass fiber residue	2.4	0.01	-	-	-

[a] Calculated by difference [b] Calculated according Shih et al. [31].

2.2. Thermolysis experiments

2.2.1. Thermal studies of the polyester fibreglass samples

The thermal behaviour of the PFG samples (granule size 100-200 μm) was studied using a Setaram Sensys Evolution 1500 thermal analysis system equipped with a differential thermal analyser (DTA) and a thermogravimetric analyser (TGA). The samples (30 mg) were heated at 800ºC (10ºC min^{-1}) in pure air (20 ml min^{-1}).

2.2.2. Thermolysis of waste polyester fibreglass

Figure 1 shows the thermolysis installation used in the present work, which consists of a heating system and a gas condensation device. The muffle furnace (1) contains a 9.6 dm^3 steel reactor, sealed by a screw-on lid. The reactor has an exit orifice for the gases generated during heating, and an orifice via which a thermocouple can be attached to measure the reactor's internal temperature. The flue gases circulate across four condensers (3-6) connected to each other by

six cooling pipes (590 mm length, 15 mm external diameter). Each condenser is a stainless steel pipe (405 mm length, 60 mm external diameter) placed at a 15º slope. This allows for the collection of the distilled oils as the gases cool. Each condenser has four collection holes for the withdrawal of the distilled liquids, and a thermometer to measure their temperature. The non-condensable gases are led to a water-cooling tower (7) where the last fraction of the distilled liquids is collected. These gases pass through a set of three filters (8 and 9) (nickel sponge, activated carbon, and a membrane filter) to eliminate pollutant gases and solid particles. The gases can then be mixed with air and burned off or collected in Tedlar plastic bags for analysis. When thermolysis is complete (the endpoint being determined via the rotameter (10) inside the tubing detecting no more distillation gas), the reactors are cooled and the thermolytic solid residues removed.

The amount of gas generated was estimated by the difference between the initial weight of PFG and the amount of liquids and solids obtained.

A typical run involved the thermolysis of about 4 kg of PFG pieces measuring 12 x 4 cm. Based on preliminary DTA/TGA studies, 550ºC was selected as the working temperature. The experiment was performed in triplicate.

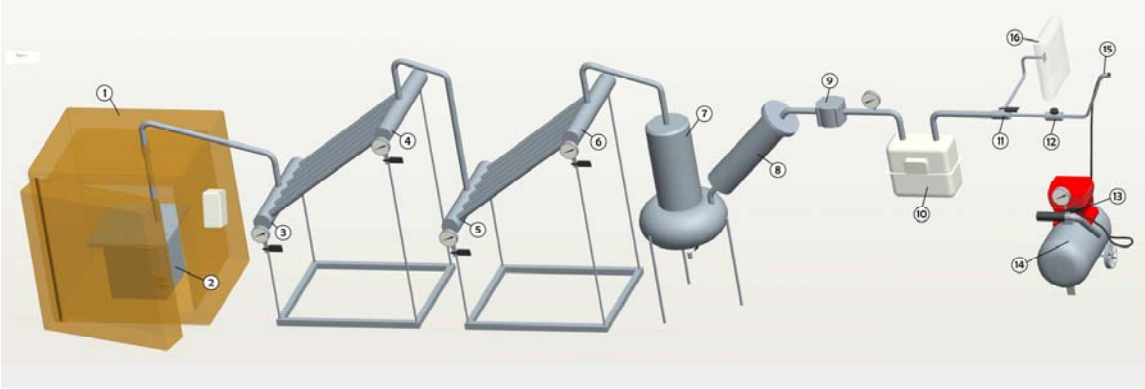

Figure 1 Installation used for the thermolysis of the PFG

2.3. Characterisation of the products of polyester fibreglass thermolysis

2.3.1. Liquid fraction (oil)

The elemental composition and GCV of the thermolysis liquid (oil) were determined using an automated LECO CHNS 923 analyser and an IKAWEEME C4000 automatic bomb calorimeter respectively. The oil product was dissolved in dichloromethane (DCM) and analyzed mainly by gas chromatography/mass spectrometry (GC/MS) using a GCMS-QP2010-Plus chromatograph (Shimadzu, Scientific Instruments) with and Teknokroma TRB-WAX (100% Polietilenglicol (PEG)) capillary column: 20 m in length, 0.1 mm diameter and 0.1 μm film thickness. The carrier gas was helium. The GC/MS oven temperature programme used for the separation of oil components was a follows: the oven was held at 40 ºC for 1 min, then ramped at 4 ºC/min to 230 ºC where it was held for a further 25 min. The MS detector was operated at full scan from was 45 to 350 amu. The ion-mass spectra derived were automatically compared to the NIST 08 spectra library and similarity of >95% were used to identify compounds. Samples were injected using an AOC-20i autoinjector (Shimadzu).

The flashpoint of the oil was estimated using a STANHOPE-SETA Setaflash 3 apparatus and a closed cup system (ASTM D1655). The kinematic viscosity was determined at 40ºC using a THERMO SCIENTIFIC Haake 1 plus viscosimeter. The water content was analysed by Karl-Fischer titration (titrant: Hydranal Composite 5K. [Fluka]) using a Karl-Fischer MKS-520 Moisture Titrator.

To obtain the distillation curves, pooled sample of the oils obtained in different runs at 550°C were subjected to automatic distillation tests using a PAC OptiDist apparatus following the ASTM D86 method at atmospheric pressure. Testing was performed from room temperature up to the temperature at which no more distillation products were collected.

2.3.2. Gases

The thermolytic gas produced was analysed by gas chromatography using a HEWLETT-PACKARD 5890 chromatograph equipped with a Porapak N and Molecular Sieve multicolumn system, a thermal conductivity detector (TCD), and a flame ionisation detector (FID). The carrier gas (0.39 MPa) was He (99.999% pure). The GCV of the dry gas was calculated according to the equation proposed by Xiao et al. [27].

2.3.3. Solid fraction

Proximal and elemental analyses of the solid residue particles were undertaken using a LECO TGA 701 and LECO CHNS 923 analyser respectively. Morphological studies of the solid residue were performed using a Hitachi model S-2100 scanning electron microscope (SEM).

2.4. Glass-ceramic production

The solid residue left after thermolysis was ground using a RETSCH PM 100 ball mill at 500 rpm for 15 min. 47.5 g of the resulting powder (particle size <250 μm) was then mixed with 4.3 g of Na_2O (from Na_2CO_3) in a Turbula blender for 30 min, placed in an aluminosilicate crucible and melted in an electric furnace at 1450°C (10°C/min) for 120 min. The molten material was then poured into water, to produce a glass frit.

This frit was then ground using a RETSCH PM 100 ball mill at 400 rpm, and 11 fractions of different sized particles separated (see Table 3) with the aim of determining the effect of particle size on glass crystallisation. The thermal stability of these different glass fractions and their preferential crystallisation mechanisms (surface or bulk) were studied by DTA employing a SETARAM LABSYS TG apparatus. DTA analyses were performed between 25°C and 1400°C in air, using calcined Al_2O_3 as a reference material. All analyses were performed at a heating rate of 50°C/min. The DTA curves were normalised to sample weight. Mineralogical study of crystalline phases devitrified by thermal treatment was performed by X-ray diffraction (XRD) using a PHILIPS X 'PERT MPD (operating at 50 kV and 30 mA) employing Cu K_α radiation.

The feasibility of the sintering + crystallization process to produce glass-ceramic tiles was evaluated on a mixture of different particle size glass powders: 1600-2000 μm, 160-250 μm and 80-100 μm. We chose to work with a mixture of different particle sizes because it leads to materials similar to natural stone. The percentages of the different fractions (1600-2000 μm (47 wt%), 160-250 μm (32 wt%) and 80-100 μm (21 wt%)) were randomly chosen. Forming by pressure with the aid of a binder is feasible when using very fine powder. In this case the majority fraction (47 wt%) is coarse (1600-2000 μm), so the most appropriate method is compaction by vibration. The mixture was compacted in a plaster mould and afterward fired at 1013°C for 60 minutes with heating and cooling rate of 50°C/min.

Table 3 Glass frit particle size fractions separated by mechanical milling and sieving.

Fraction	Particle size range (μm)
f1	2000-5000
f2	1600-2000
f3	1000-1600
f4	500-1000
f5	400-500
f6	250-400
f7	160-250
f8	100-160
f9	80-100
f10	63-80
f11	< 63

3. Results and Discussion

3.1. Thermal studies of the polyester fibreglass samples

Figure 2 shows the TG/DTG curves for the thermal degradation of PFG waste in air. Table 4 shows the peak temperatures and mass losses for the different degradation phases. The first phase (dehydration) temperature peak occurs at around 210ºC. The second and main phase of degradation temperature peak occurs between 259ºC and 392ºC. In the isophthalic acid-based polyester resin the second step involves scission at the cross-link and formation of styrene and the linear polyester which subsequently breaks randomly [28-32]. The third phase (formation of primary carbonaceous material or char) peak occurs at around 449ºC. The formation of char is due to secondary repolymerization reactions among the polymer derived products. The total mass loss over the temperature interval 20-800ºC was 32.6 wt%.

3.2. Thermolysis of the polyester fibreglass samples

3.2.1. Thermolytic yields

The yield of solid residue was 68.1 ± 0.8 wt%; the oil and gas fractions accounted for 23.9 ± 0.1 wt% and 8.0 ± 0.9 wt% respectively. The liquid + gas yield (31.9 ± 0.8 wt%) was somewhat lower than the theoretical value that should be expected from table 1. The difference may be attributed to char formation.

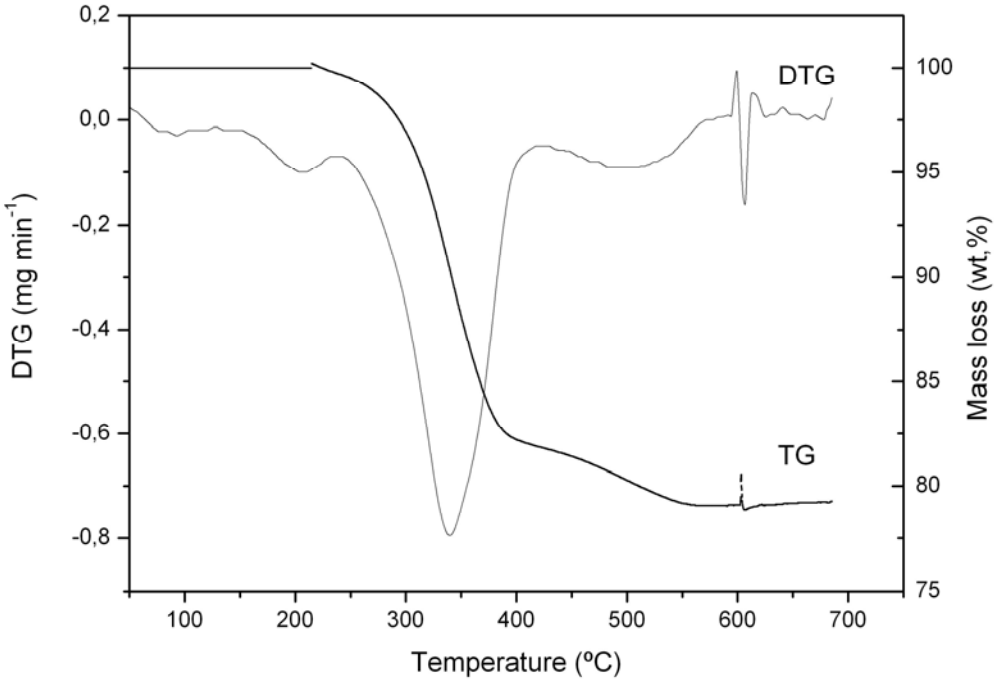

Figure 2 TG/DTG curves for PFG waste when thermally degraded in air.

Table 4 Characteristic temperatures of the three degradation phases of PFG waste in air.

Step 1		Step 2		Step 3	
Peak Temperature (ºC)	Mass loss (wt%)	Peak Temperature (ºC)	Mass loss (wt%)	Peak Temperature (ºC)	Mass loss (wt%)
209.8	1.8	334.6	26.4	448.7	4.4

3.2.2. Characteristics of the solid residue

The solid residue obtained by thermolysis was composed of pieces of dimensions equal to those of the input material, but completely black (Figure 3).

Figure 4 shows the microstructure of the initial PFG waste (a) and the glass fibre after thermolysis at 550ºC (b). Char can be seen on the surface of the fibres. It has been reported [3,16,23] that a certain amount of char or coke-like material is formed during the pyrolysis of many polymeric materials due to secondary repolymerisation reactions in the gaseous phase.

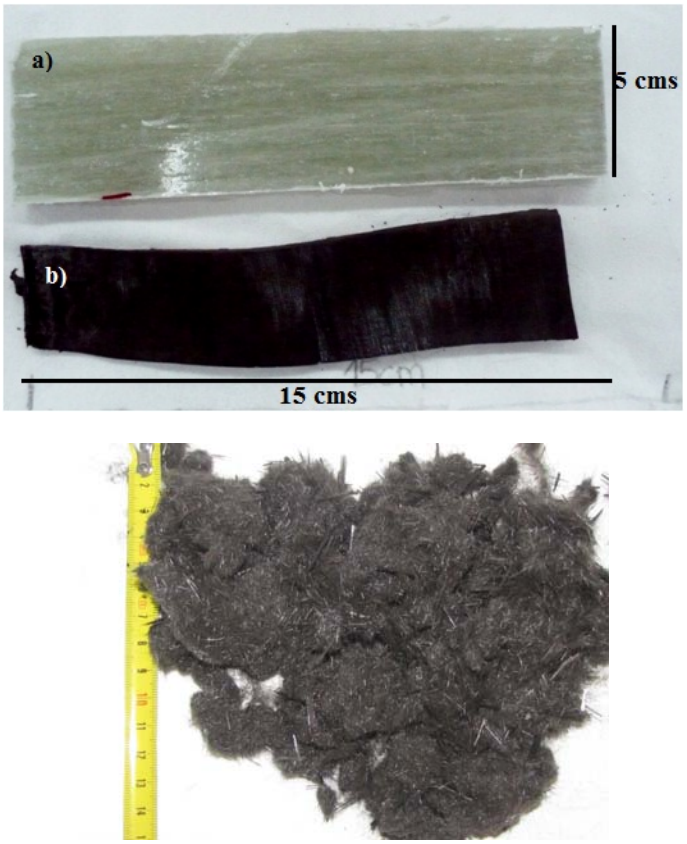

Figure 3 (a) PFG fragment, (b) glass fibre obtained after thermolysis, (c) glass fibre obtained after grinding.

The amount of char formed in the thermolysis process was analysed by TGA of the solid residue at 700ºC in O_2, and recorded as about 2.9 wt%.

The inorganic matter in the solid thermolysis residue calculated according to the equation proposed by Torres et al. [24] corresponded to 65 wt%, in agreement with the composition of the PFG waste (Table 1). This confirms that the polyester resin was fully decomposed at the 550ºC thermolytic temperature used.

The thermolysis solid residue was essentially composed of 97 wt% glass fibre and 3 wt% char (from secondary repolymerisation reactions). The char does not interfere in the process of obtention of glass-ceramic materials. The vitrification process removes this char and burnt it and therefore it does not interfere in the process.

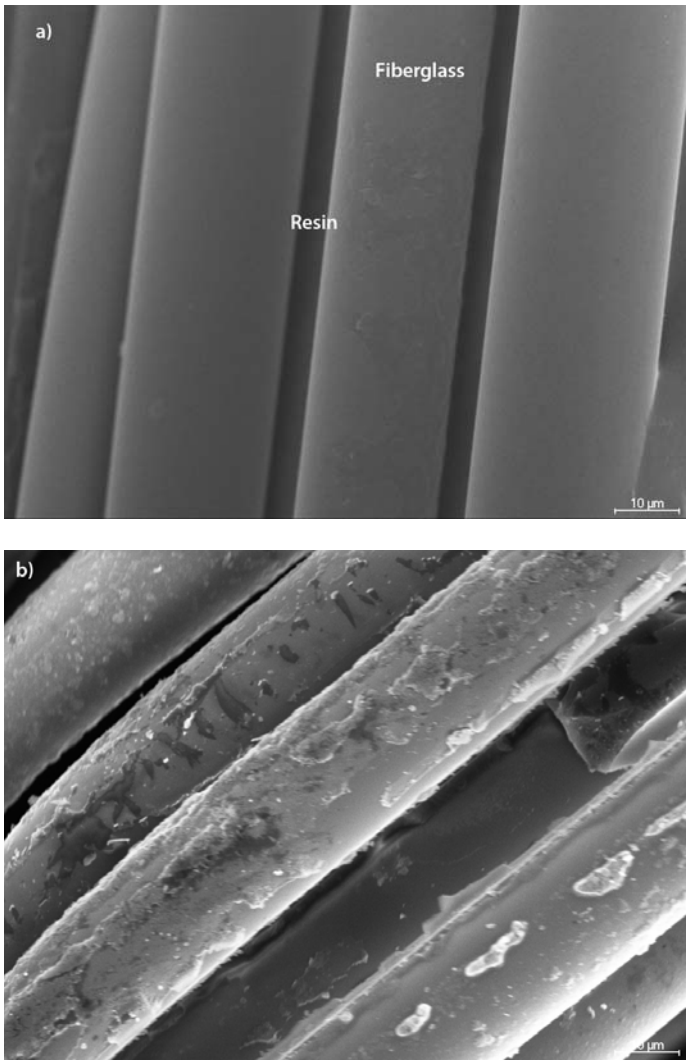

Figure 4 SEM images showing glass fibres (a) in the PFG waste and (b) after thermolysis.

Table 2 shows the carbon content in the glass fibre residue to reach 2.4 wt%. This content is very similar to the 2.5-3.6 wt% indicated by Torres et al. [24] after the pyrolysis of SMC at 500ºC. However, it is much lower than that obtained by Pickering (16 wt%) [3].

3.2.3. Oil characterisation

The H/C atomic ratio of the distilled oil was rather low (≈1.2), indicating it to be mainly aromatic in nature. Its GCV, 33.9 MJ kg^{-1}, is similar to that of a fuel oil (Table 5).

Table 5 Elemental composition (wt%), H/C atomic ratio and gross calorific value (MJ kg^{-1}) of the oil obtained at 550ºC.

C (wt%)	H (wt%)	O (wt%)	N (wt%)	H/C ratio	GCV (MJ kg^{-1})	Density at 20ºC (kg m^{-3})	Viscosity at 40 ºC (cSt)	Flash point (ºC)
75.2	7.5	16.1	0.1	1.2	33.9	0.94	1.77	< 20

The oil is in fact a mixture of organic compounds and aqueous products. The water content was 2.4 wt%, whereas the water content of the original PFG was 0.5 wt%. Taking into account mass loss by dehydration determined from the TGA curve (1.8 wt%), the 2.4 wt% water content of the oil results from the inherent PFG moisture and the water generated by the breakage of oxygenated organic compounds during thermolysis. Similar results have previously been reported [12,34-36].

The compounds tentatively identified in the GC/MS chromatogram, and the subsequent comparison of the relative areas under each peak, clearly show the predominantly aromatic nature of the oil. Table 6 summarises the major fractions of volatile organic compounds. The oil is thus a complex mixture of C_5-C_{21} organic compounds, basically of aromatic structure (≈84%), plus a relatively high content of oxygenated species (≈16%).

As shown in Table 6, the major PFG degradation product was styrene. Toluene, ethylbenzene, α-methyl styrene and 3-butynyl benzene were also detected. The polyester portion of PFG waste degraded mostly into benzoic acid and 1,2-benzenedicarboxylic acid anhydride (o-phthalic acid anhydride). The formation of the 1,2-benzenedicarboxylic acid anhydride involves alkyl-oxygen scission of the polyester chain. The carboxylate group (COO^-) generated can react with the adjacent ester group to form the acid anhydride [37]. The formation of the benzoic acid - from polystyrene resin containing β hydrogen atoms - involves alkyl-oxygen scission via a six-membered transition state to produce a carboxylic acid and a vinyl ester. The structure of the vinyl ester produced from the polyester resin is dependent upon the type of alcohol used to prepare the polyester. The presence of benzoic acid in the oil indicates that propanediol was used in the preparation of the polyester.

Table 6 Tentative characterisation of the oil obtained by PFG thermolisis at 550ºC (quantitative estimation based on the relative area under each peak).

Peak nº	Retention time (min)	Peak area (%)	Compounds
1	5.968	0.94	Benzene
2	6.271	0.26	1,3-Dioxolane, 2-methyl
3	6.407	0.17	2-(2-Methoxyethoxy)ethyl acetate
4	6.916	0.01	di-tert-Butyl dicarbonate
6	8.04	1.60	1,3-Dioxolane, 2-ethyl-4-methyl
7	8.398	9.50	Toluene
8	8.556	2.40	Hexane, 3-methoxy
9	9.001	0.02	Cyclopropane, propyl
10	9.157	0.08	1,4-Dioxane
11	9.711	0.00	Methylglyoxal
12	10.713	0.79	2-Propen-1-ol
13	10.928	15.00	Ethylbenzene
14	11.318	0.01	Ethylbenzene
15	12.025	0.10	Furan, 2,5-dihydro-3,4-dimethyl
16	12.351	3.24	Benzene, (1-methylethyl)
17	12.566	0.11	Propanoic acid, 2-allyloxy-, ethyl ester
18	12.717	0.01	Oxalic acid, butyl propyl ester
19	13.121	0.02	Propanoic acid, 2-hydroxy-2-methyl
20	13.411	0.54	Benzene, propyl
21	14.429	0.29	1-Propene, 3,3',3"-[methylidynetris(oxy)]tris
22	14.908	25.77	Styrene
23	15.116	0.31	Benzene, 1-ethenyl-4-methyl
24	16.537	0.40	Benzene, butyl
25	17.084	7.63	alpha.-Methylstyrene
26	17.292	0.02	Ethanone, 2-(5-nitrotetrazol-2-yl)-1-phenyl-
27	17.917	0.85	2-Benzyloxyphenylacetonitrile
28	18.843	0.27	1,3,5-Cycloheptatriene, 7,7-dimethyl
29	19.208	0.50	o-Methylstyrene
30	22.703	0.40	Benzaldehyde
31	25.778	0.23	Ethanone, 2,2-dihydroxy-1-phenyl
32	26.056	0.26	Acetophenone
33	26.333	0.17	Benzoylformic acid
34	29.379	0.11	Benzoic acid, 2-(benzoylthio)thiazol-4-yl ester
35	29.933	0.54	Ethanedione, diphenyl
36	30.151	0.08	Benzamide, 4-benzoyl-N-(immino)(methylthio)
37	31.678	0.22	Naphthalene, 1-methyl
38	33.837	0.30	Acenaphthene
39	36.054	0.16	Naphthalene, 1-(2-propenyl)
40	36.229	0.42	Benzyl sulfone
41	39.001	0.71	Benzene, 1,1'-(1-methyl-1,3-propanediyl)bis
43	40.219	3.00	Dimethyl phthalate or pthalic acid
44	41.314	1.51	Benzene, 3-butynyl
45	43.024	4.30	Benzoic acid
46	43.415	2.52	1,2-Diphenylcyclopropane

The oil contained about 27% styrene. Thus, this oil has potential as a feedstock for the manufacture of polyester resin.

Figure 5 shows the results obtained for the oil in the automatic distillation test. The initial boiling point of the oil was 69.8ºC and the final boiling point 340.7ºC. Some 50% of the volume of the oil has a boiling point between 70º and 251ºC, which falls into the range of commercial gasoline. The remaining 50 wt% , contained compounds with a boiling point between 251ºC and 340.7ºC, and could be used as heating fuel when mixed with commercial fuel oils.The distillation residue represented 2 vol% of the initial sample.

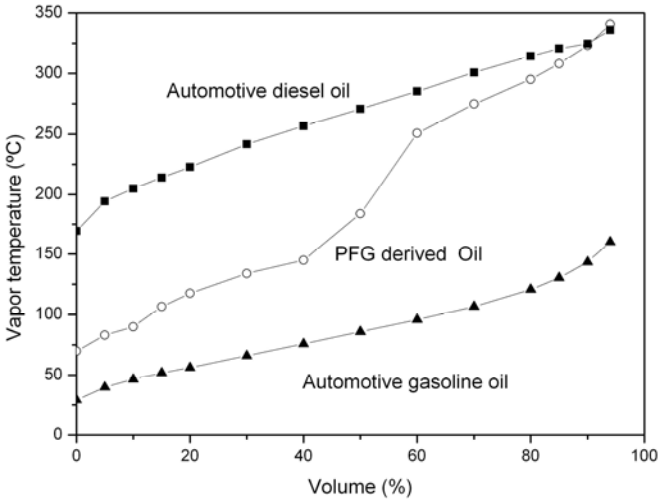

Figure 5 Distillation data for poliested fiber glass derived-oil, automotive diesel and gasoline oils.

3.2.4. Gas characterisation

The gas produced in PFG thermolysis (Table 7) was mostly a mixture of CO_2 and CO; the hydrocarbon fraction was below 10 vol%. This gas had a gross calorific value (GCV) of about 26 MJ Nm^{-3}; similar results have been reported by other authors [11,12,38]. This value is rather low for it to be used to as a fuel for gas turbines; a value of >40 MJ Nm^{-3} and greater contents of H_2 and CH_4 are usually required. However, this gas is suitable for heating the thermolysis reactor.

Other composite residues containing a greater resin content or resins other than polyester (e.g., vinylester, phenolic, urea formaldehyde or epoxy resin), would yield gases with higher GCVs and greater H_2 contents. These could certainly be revalorised as gas turbine fuels. Jie et al. [23] produced gases with 38.5% H_2 and 15% C_1-C_4 hydrocarbons from the pyrolysis of printed circuit boards containing epoxy resins.

Table 7 Composition (vol%) and gross calorific value (MJ Nm^{-3}) of the thermolytically-produced gases.

Gas	Vol.%
H_2	2.30
O_2	1.51
N_2	6.76
CO	21.46
CO_2	37.51
CH_4	8.97
C_2H_4 (ethene)	3.69
C_2H_6 (ethane)	7.98
C_3H_6 (propene)	6.50
C_3H_8 (propane)	0.69
nC_4H_{10} (n-butane)	1.71
$isoC_4H_{10}$ (isobutane)	0.27
H_2S	n.d.
NH_3	n.d.
GCV (MJ Nm^{-3})	26.0

3.3. Glass characterization

Figure 6 depicts the DTA curves of both powdered (<63 μm) and bulk glass produced from the post-thermolysis solid residue, and for the different size fractions. As expected, both curves (Fig 6a) show a glass transition, *Tg*, at 672ºC, because this temperature is independent of glass particle size and it is just related to glass composition and to the cooling rate from melting temperature. DTA thermogram of powder glass sample shows two distinct crystallization

exothermic peaks at 818º and 1013°C respectively, followed by two endothermic reactions indicating formation of liquid phases. In contrary, DTA curve recorded on bulk glass sample shows no exothermic peaks, indicating that bulk glass is thermally stable and crystallization by heating does not occur. This behavior indicates that after subsequent thermal treatments, the glass will devitrify through a surface crystallization mechanism and therefore, the most appropriate method for glass-ceramic materials production will be through a sintering + crystallization.

To assess the effect of particle size on crystallization, Figure 6b and 6c shows the DTA curves recorded on the different particle size fractions (Table 3). It is noted that increasing particle size leads to a decrease in the height of crystallization peaks (Figure 6c), which even disappear from the curve recorded on 1000-1600 μm fraction (Figure 6b). The exothermic peak centered at 818°C is undetectable in fractions with particle size larger than 100 μm, whereas crystallization peak at 1013°C is not perceptible for particles above 1000 μm. Consequently, DTA curves recorded on particles larger than 1000 μm do not show any exothermic peak, indicating that these fractions are very stable against crystallization. These results verify that surface crystallization plays a major role in crystallization of the present glass. Similar findings have been reported for other materials [39-42].

Figure 7 shows the X-ray diffractogram of powder glass sample after thermal treatment at 1013ºC for 60 min. Glass devitrification leads to a glass-ceramic material composed of wollastonite ($CaSiO_3$) and plagioclase s.s., which corresponds to a series of solid solution between albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) end-members.

Figure 8 illustrates the appearance of both the glass frit derived from the thermolytic solid residue (Figure 8a) and the glass-ceramic tile obtained by sintering+ crystallization of a mixture of different particle size glass powders at 1013ºC for 60 min (Figure 8b). It is noted that the glass particles reach an appropriate degree of sintering during heating, resulting in a compact tile. Glass grains with particle size lower than 250 μm crystallize during firing and give rise to an opaque ceramic material, whose crystalline phases scatter visible light. By contrast, larger glass particles (>1600 μm) are thermally stable and therefore, maintain a high degree of transparency. The combination of matt crystalline region and transparent amorphous grains results in a glass-ceramic material with an aesthetic similar to natural stone. It appears that it could be suitable as ceramic tile for wall covering or floor pavement.

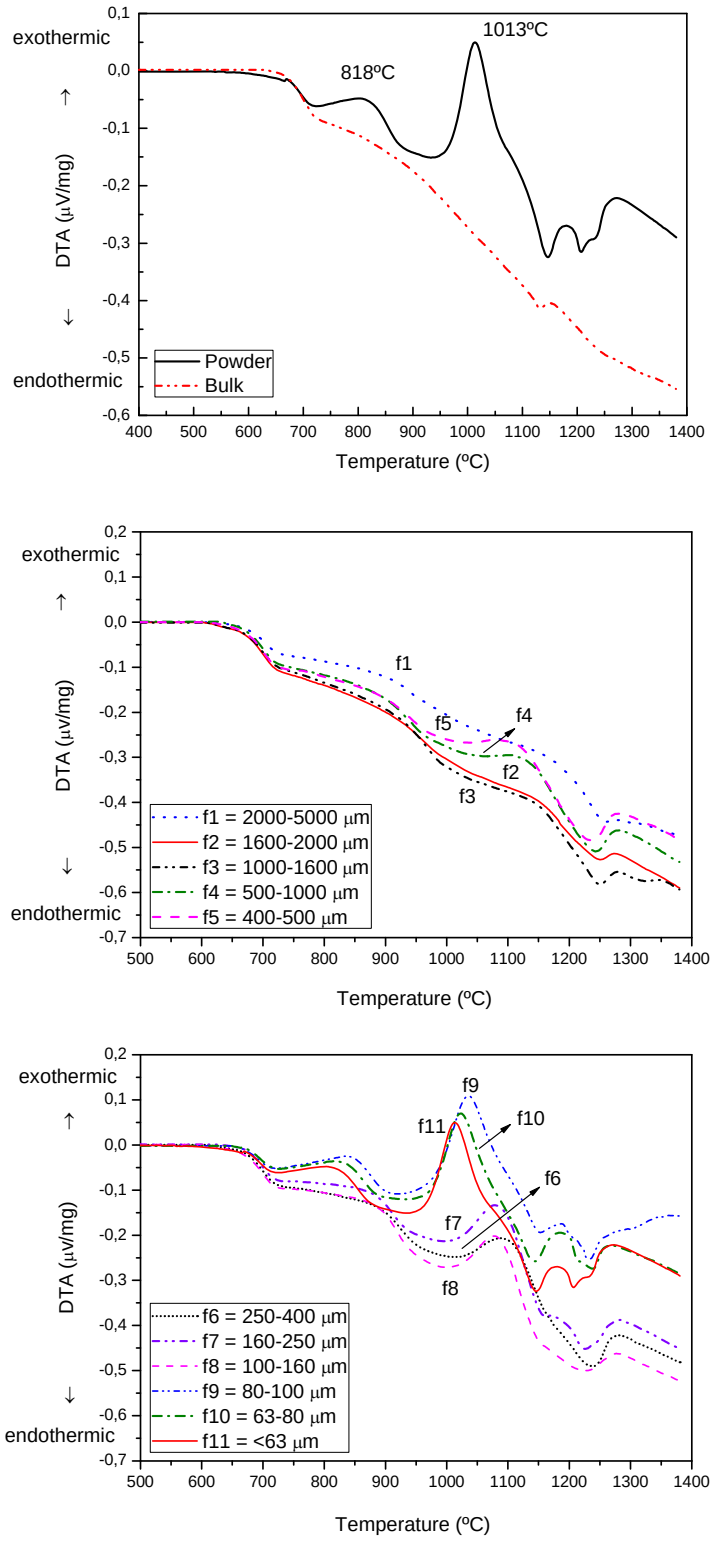

Figure 6 DTA curves for bulk and powder glass samples (25º-1450ºC, 50ºC min-1): (6a) powder (f11) and bulk, (6b) f1-f5, (6c) f6-f11.

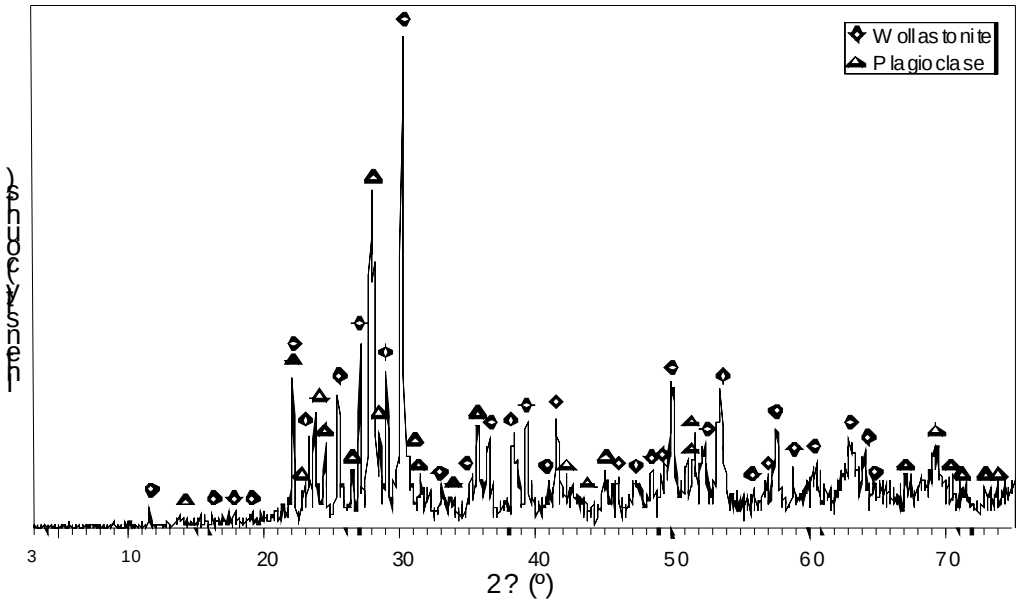

Figure 7 X-ray diffraction patterns for the glass-ceramic material produced by thermal treatment of the powder glass (T = 1013ºC, t = 60 min).

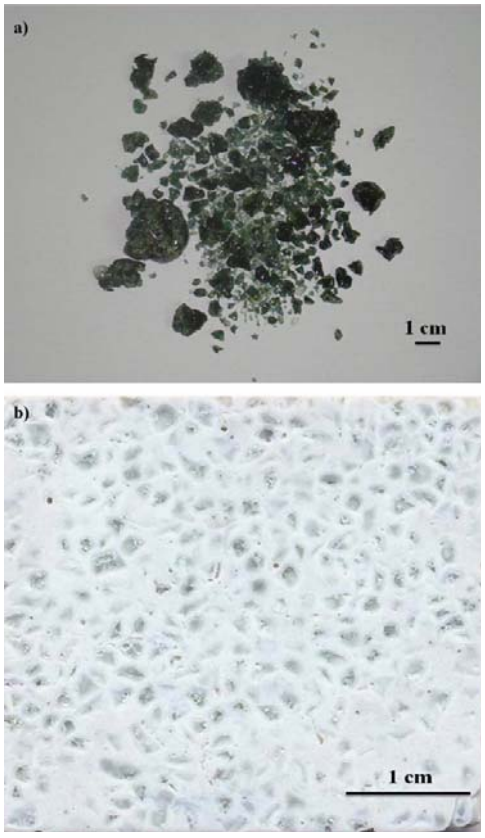

Figure 7 X-ray diffraction patterns for the glass-ceramic material produced by thermal treatment of the powder glass (T = 1013ºC, t = 60 min).

A study to optimise the particle size mixture is currently underway. The main goal is to tailor the firing process to the conventional fast-firing schedule used in ceramic tile manufacture. The technological properties of these glass-ceramic tiles will also be determined to establish the feasibility of their use as ceramic building materials.

CONCLUSIONS

This laboratory-scale study suggests that thermolysis is a highly suitable method for recovering valuable products and energy from PFG. The results allow the following conclusions to be drawn:

(1) The thermolysis of the present PFG resulted in 68 wt% solid residue; the liquid (oil) and gas fractions accounted for 24 wt% and 8.0 wt% respectively.

(2) The oil fraction is a complex mixture of C_5-C_{21} compounds, basically of aromatic structure (≈ 84%), plus a high content of oxygenated species (≈16%). The oil mostly consists of styrene (≈27%). Other products such as toluene, ethylbenzene, α-methyl styrene, 3-butynil benzene, benzoic acid and 1,2-benzenedicarboxylic acid anhydride (anhydride of o-phthalic acid) are also present. The GCV of the oil, 33.9 MJ kg^{-1}, is similar to that of a fuel oil. Some 50% of the liquid volume has a boiling point between 70º and 194ºC, which falls into the range of commercial petroleum.

(3) The gas produced was mostly CO_2 and CO; the hydrocarbon fraction made up <10 vol%. The gross calorific value of the gas was low, at about 26 MJ Nm^{-3}.

(4) The solid residue consisted of 97 wt.% glass fibre and 3 wt.% carbonaceous material. The glass fibre was successfully recycled by a vitrification process. Size fractions of >1000 μm showed low glass-ceramic-forming ability. The crystalline phases identified in the glass-ceramic material obtained from the finest particle fraction (f11; <63 μm) were wollastonite and plagioclase s.s.

(5) Compact glass-ceramic tiles can be produced from the powder glass via sintering-crystallisation. By varying the relative percentage of the different particle size fractions, tiles with different aesthetic qualities might be designed.

(6) The novel thermolytic and vitrification processes described in this work hold promise for recycling fibreglass-reinforced composite materials. The SMC and BMC composites, which contain filler, mainlyCaCO3, can also be treated by this process. These fillers should not be separated from the fiberglass. $CaCO_3$ is beneficial because it is a common component in the formation of glass.

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